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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>4</sup> :</b> C07C 55/00, 69/34 C07D 307/34, C10M 129/93	<b>A1</b>	<b>(11) International Publication Number:</b> WO 91/04959 <b>(43) International Publication Date:</b> 18 April 1991 (18.04.91)
<b>(21) International Application Number:</b> PCT/US89/04282 <b>(22) International Filing Date:</b> 29 September 1989 (29.09.89)  <b>(71) Applicant:</b> CHEVRON RESEARCH COMPANY [US/ US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).  <b>(72) Inventor:</b> RUHE, William, R., Jr. ; 895 Rose Drive, Benicia, CA 94510 (US).  <b>(74) Agents:</b> CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).  <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent)*, DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).		<b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR PREPARING POLYMERIC DISPERSANTS HAVING ALTERNATING POLYALKYLENE AND SUCCINIC GROUPS  <b>(57) Abstract</b>  A process for preparing an oligomeric copolymer of an unsaturated acidic reactant and a high molecular weight olefin having a sufficient number of carbon atoms such that the resulting copolymer is soluble in lubricating oil and wherein at least 20 weight percent of the total olefin comprises an alkylvinylidene isomer, which process comprises reacting the high molecular weight olefin with the unsaturated acidic reactant in the presence of a solvent which comprises the reaction product of an unsaturated acidic reactant and a high molecular weight olefin.		

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01           PROCESS FOR PREPARING POLYMERIC DISPERSANTS  
02           HAVING ALTERNATING POLYALKYLENE AND SUCCINIC GROUPS

03  
04                   BACKGROUND OF THE INVENTION  
05

06   The present invention relates to a process for preparing  
07   compositions which are useful as intermediates for dis-  
08   persants used in lubricating oil compositions or as dis-  
09   persants themselves. In addition, some of the compositions  
10   prepared by the present process are useful in the pre-  
11   paration of high molecular weight dispersants which have  
12   superior dispersant properties for dispersing sludge and  
13   varnish and superior Viton Seal compatibility. Such high  
14   molecular weight dispersants also advantageously impart  
15   fluidity modifying properties to lubricating oil composi-  
16   tions which are sufficient to allow elimination of some  
17   proportion of viscosity index improver from multigrade  
18   lubricating oil compositions which contain these  
19   dispersants.

20  
21   It is known in the art that alkenyl-substituted succinic  
22   anhydrides have been used as dispersants. Such alkenyl-  
23   substituted succinic anhydrides have been prepared by two  
24   different processes, a thermal process (see, e.g., U.S.  
25   Patent No. 3,361,673) and a chlorination process (see, e.g.,  
26   U.S. Patent No. 3,172,892). The polyisobutenyl succinic  
27   anhydride ("PIBSA") produced by the thermal process has been  
28   characterized as a monomer containing a double bond in the  
29   product. Although the exact structure of chlorination PIBSA  
30   has not been definitively determined, the chlorination  
31   process PIBSA materials have been characterized as monomers  
32   containing either a double bond, a ring other than a  
33   succinic anhydride ring and/or chlorine in the product.  
34   [See J. Weill and B. Sillion, "Reaction of Chlorinated

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01 Polyisobutene with Maleic Anhydride: Mechanism Catalysis by  
02 Dichloromaleic Anhydride", Revue de l'Institut Français du  
03 Pétrole, Vol. 40, No. 1, pp. 77-89 (January-February,  
04 1985).] Such compositions include one-to-one monomeric  
05 adducts (see, e.g., U.S. Patents Nos. 3,219,666; 3,381,022)  
06 as well as adducts having polyalkenyl-derived substituents  
07 adducted with at least 1.3 succinic groups per polyalkenyl-  
08 derived substituent (see, e.g., U.S. Patent No. 4,234,435).  
09

10 In addition, copolymers of maleic anhydrides and some ali-  
11 phatic alpha-olefins have been prepared. The polymers so  
12 produced were useful for a variety of purposes including  
13 dispersants for pigments and intermediates in the prepara-  
14 tion of polyesters by their reaction with polyols or poly-  
15 epoxides. However, olefins having more than about 30 carbon  
16 atoms were found to be relatively unreactive. (See, e.g.,  
17 U.S. Patents Nos. 3,461,108; 3,560,455; 3,560,456;  
18 3,560,457; 3,580,893; 3,706,704; 3,729,450; and 3,729,451).  
19

20 Commonly assigned copending U.S. patent application Serial  
21 No. 251,613, to James J. Harrison, filed September 29, 1988,  
22 entitled "Novel Polymeric Dispersants Having Alternating  
23 Polyalkylene and Succinic Groups" discloses copolymers pre-  
24 pared by reacting an unsaturated acidic reactant, such as  
25 maleic anhydride, with a high molecular weight olefin, such  
26 as polyisobutene, in the presence of a free radical initia-  
27 tor, wherein at least about 20 percent of the total high  
28 molecular weight olefin comprises an alkylvinylidene isomer  
29 and wherein the high molecular weight olefin has a suffi-  
30 cient number of carbon atoms such that the resulting copolymer  
31 is soluble in lubricating oil. In U.S. Serial No. 251,613,  
32 it is also taught that the reaction may be conducted neat or  
33 in the presence of a solvent in which the reactants and free  
34 radical initiator are soluble. Suitable solvents disclosed

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01 in U.S. Serial No. 251,613 include liquid saturated or  
02 aromatic hydrocarbons having from 6 to 20 carbon atoms,  
03 ketones having from 3 to 5 carbon atoms and liquid saturated  
04 aliphatic dihalogenated hydrocarbons havng from 1 to 5  
05 carbon atoms. Examples of solvents taught in U.S. Serial  
06 No. 251,613 are acetone, tetrahydrofuran, chloroform,  
07 methylene chloride, dichloroethane, toluene, dioxane,  
08 chlorobenzene and xylene.

09

10 The use of halogenated hydrocarbons as a solvent in the  
11 reaction of unsaturated acidic reactants, such as maleic  
12 anhydride, and high molecular weight olefins of the type  
13 described in U.S. Serial No. 251,613 has a number of  
14 disadvantages. Such solvents are expensive, they are  
15 environmentally undesirable and they impede recycling of  
16 lubricating oils because of the residual halogen content.

17

18 In the above-described reaction, the solvent is used  
19 primarily to solubilize the unsaturated acidic reactant, but  
20 also serves to reduce the viscosity of the reaction mixture.  
21 Unsaturated acidic reactants such as maleic anhydride are  
22 not very soluble in high molecular weight olefins at typical  
23 reaction temperatures of 50°C to 210°C. When the unsatu-  
24 rated acidic reactant is maleic anhydride, it has been found  
25 that if the maleic anhydride forms a separate phase due to  
26 poor solubility, not only is the reaction rate negatively  
27 affected, but an undesirable resin or tar-like substance is  
28 formed which is believed to be polymaleic anhydride. Conse-  
29 quently, it would be highly advantageous to provide a pro-  
30 cess which avoids this condition, without having to resort  
31 to a halogenated hydrocarbon solvent.

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SUMMARY OF THE INVENTION

01  
02  
03 The present invention is directed to a process for preparing  
04 an oligomeric copolymer of an unsaturated acidic reactant  
05 and a high molecular weight olefin having a sufficient num-  
06 ber of carbon atoms such that the resulting copolymer is  
07 soluble in lubricating oil and wherein at least 20 weight  
08 percent of the total olefin comprises an alkylvinylidene  
09 isomer, which process comprises reacting the high molecular  
10 weight olefin with the unsaturated acidic reactant in the  
11 presence of a free radical initiator and a solvent which  
12 comprises the reaction product of an unsaturated acidic  
13 reactant and a high molecular weight olefin. Preferably,  
14 the solvent comprises (a) an oligomeric copolymer of an  
15 unsaturated acidic reactant and a high molecular weight  
16 olefin; or (b) a monomeric adduct of an unsaturated acidic  
17 reactant and a high molecular weight olefin in at least a  
18 one to one mole ratio of acidic reactant to olefin; or a  
19 mixture thereof.  
20  
21 The copolymers produced by the present process have alter-  
22 nating succinic and polyalkylene groups. Suitable olefins  
23 for use in preparing these copolymers include those having  
24 about 32 carbon atoms or more, preferably having about 52  
25 carbon atoms or more. Those preferred high molecular weight  
26 olefins include polyisobutenes. Especially preferred ole-  
27 fins for use in preparing the copolymer products are poly-  
28 isobutenes having average molecular weights of from about  
29 500 to about 5000 and in which the alkylvinylidene isomer  
30 comprises at least 50 percent of the total olefin.  
31  
32 The copolymers prepared by the process of the invention are  
33 useful as dispersants themselves and also as intermediates  
34 in the preparation of other dispersant additives having

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01 improved dispersancy and/or detergency properties when  
02 employed in a lubricating oil. These copolymers are also  
03 advantageous because they do not contain double bonds, rings  
04 other than succinic anhydride rings, or chlorine (in  
05 contrast to thermal and chlorination PIBSAs) and as such  
06 have improved stability, as well as improved environmental  
07 properties due to the absence of chlorine.

08

09 The copolymers produced by the instant process can also be  
10 used to form polysuccinimides which are prepared by reacting  
11 the copolymer with a polyamine to give a polysuccinimide.  
12 Such polysuccinimides include mono-polysuccinimides (where a  
13 polyamine component reacts with one succinic group); bis-  
14 polysuccinimides (where a polyamine component reacts with a  
15 succinic group from each of two copolymer molecules, thus  
16 effectively cross-linking the copolymer molecules); and  
17 higher polysuccinimides (where a polyamine component reacts  
18 with a succinic group from each of greater than 2 copolymer  
19 molecules). These polysuccinimides are useful as disper-  
20 sants and/or detergents in fuels and oils. In addition,  
21 these polysuccinimides have advantageous viscosity modifying  
22 properties, and may provide a viscosity index credit  
23 ("V.I. Credit") when used in lubricating oils, which may  
24 permit elimination of some portion of viscosity index  
25 improver ("V.I. Improver") from multigrade lubricating oils  
26 containing the same.

27

28 In addition, such polysuccinimides can form a ladder poly-  
29 meric structure or a cross-linked polymeric structure.  
30 These structures are advantageous because it is believed  
31 such structures are more stable and resistant to hydrolytic  
32 degradation and also to degradation by shear stress.

33

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01 Moreover, the copolymers prepared by the present process can  
02 be employed to make modified polysuccinimides wherein one or  
03 more of the nitrogens of the polyamine component is sub-  
04 stituted with a hydrocarbyl oxycarbonyl, a hydroxyhydrocar-  
05 byl oxycarbonyl or a hydroxy poly(oxyalkylene)-oxycarbonyl.  
06 These modified polysuccinimides are improved dispersants  
07 and/or detergents for use in fuels or oils.  
08

09 Accordingly, the copolymers made by the present process are  
10 useful in providing a lubricating oil composition comprising  
11 a major amount of an oil of lubricating viscosity and an  
12 amount of a copolymer, polysuccinimide or modified succini-  
13 mide additive sufficient to provide dispersancy and/or  
14 detergency. These additives may also be formulated in  
15 lubricating oil concentrates which comprise from about 90 to  
16 about 50 weight percent of an oil of lubricating viscosity  
17 and from about 10 to about 50 weight percent of the  
18 additive.  
19

20 Furthermore, the copolymers formed by the present process  
21 can be used to provide a fuel composition comprising a major  
22 portion of a fuel boiling in a gasoline or diesel range and  
23 an amount of copolymer, polysuccinimide or modified succini-  
24 mide additives sufficient to provide dispersancy and/or  
25 detergency. These additives can also be used to make fuel  
26 concentrates comprising an inert stable oleophilic organic  
27 solvent boiling in the range of about 150°F to about 400°F  
28 and from about 5 to about 50 weight percent of such  
29 additive.  
30

### 31 Definitions

32  
33 As used herein, the following terms have the following  
34 meanings unless expressly stated to the contrary.

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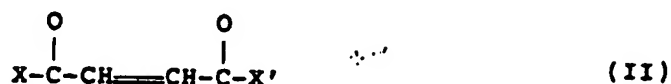
01 The term "unsaturated acidic reactants" refers to maleic or  
02 fumaric reactants of the general formula:

03

04

05

06



07 wherein X and X' are the same or different, provided that at  
08 least one of X and X' is a group that is capable of reacting  
09 to esterify alcohols, form amides or amine salts with ammo-  
10 nia or amines, form metal salts with reactive metals or  
11 basically reacting metal compounds and otherwise function as  
12 acylating agents. Typically, X and/or X' is -OH, -O-hydro-  
13 carbyl, -OM<sup>+</sup> where M<sup>+</sup> represents one equivalent of a metal,  
14 ammonium or amine cation, -NH<sub>2</sub>, -Cl, -Br, and taken together  
15 X and X' can be -O- so as to form an anhydride. Preferably  
16 X and X' are such that both carboxylic functions can enter  
17 into acylation reactions. Maleic anhydride is a preferred  
18 unsaturated acidic reactant. Other suitable unsaturated  
19 acidic reactants include electron-deficient olefins such as  
20 monophenyl maleic anhydride; monomethyl, dimethyl, mono-  
21 chloro, monobromo, monofluoro, dichloro and difluoro maleic  
22 anhydride; N-phenyl maleimide and other substituted  
23 maleimides; isomaleimides; fumaric acid, maleic acid, alkyl  
24 hydrogen maleates and fumarates, dialkyl fumarates and  
25 maleates, fumaronilic acids and maleanic acids; and  
26 maleonitrile, and fumaronitrile.

27

28 The term "alkylvinylidene" or "alkylvinylidene isomer"  
29 refers to high molecular weight olefins and polyalkylene  
30 components having the following vinylidene structure

31

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01 wherein R is alkyl or substituted alkyl of sufficient chain  
02 length to give the resulting molecule solubility in  
03 lubricating oils and fuels, thus R generally has at least  
04 about 30 carbon atoms, preferably at least about 50 carbon  
05 atoms and  $R_v$  is lower alkyl of about 1 to about 6 carbon  
06 atoms.

07

08 The term "soluble in lubricating oil" refers to the ability  
09 of a material to dissolve in aliphatic and aromatic hydro-  
10 carbons such as lubricating oils or fuels in essentially all  
11 proportions.

12

13 The term "high molecular weight olefins" refers to olefins  
14 (including polymerized olefins having a residual unsatura-  
15 tion) of sufficient molecular weight and chain length to  
16 lend solubility in lubricating oil to their reaction prod-  
17 ucts. Typically olefins having about 32 carbons or greater  
18 (preferably olefins having about 52 carbons or more)  
19 suffice.

20

21 The term "high molecular weight polyalkyl" refers to poly-  
22 alkyl groups of sufficient molecular weight and hydrocarbyl  
23 chain length that the products prepared having such groups  
24 are soluble in lubricating oil. Typically these high  
25 molecular weight polyalkyl groups have at least about 30  
26 carbon atoms, preferably at least about 50 carbon atoms.  
27 These high molecular weight polyalkyl groups may be derived  
28 from high molecular weight olefins.

29

30 The term "PIBSA" is an abbreviation for polyisobutenyl  
31 succinic anhydride.

32

33 The term "polyPIBSA" refers to a class of copolymers within  
34 the scope of the present invention which are copolymers of

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01 polyisobutene and an unsaturated acidic reactant which have  
 02 alternating succinic groups and polyisobutyl groups.  
 03 PolyPIBSA has the general formula

04

05

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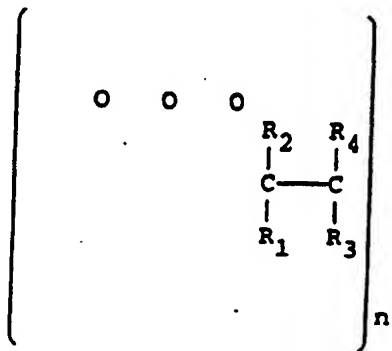
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14



15 wherein n is one or greater; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are selected from  
 16 hydrogen, methyl and polyisobutyl having at least about 30 carbon  
 17 atoms (preferably at least about 50 carbon atoms) wherein either  
 18 R<sub>1</sub> and R<sub>2</sub> are hydrogen and one of R<sub>3</sub> and R<sub>4</sub> is methyl and the  
 19 other is polyisobutyl, or R<sub>3</sub> and R<sub>4</sub> are hydrogen and one of R<sub>1</sub>  
 20 and R<sub>2</sub> is methyl and the other is polyisobutyl.

21

22 The term "PIBSA number" refers to the anhydride (succinic group)  
 23 content of polyPIBSA on a 100% actives basis. The PIBSA number  
 24 is calculated by dividing the saponification number by the per-  
 25 cent polyPIBSA in the product. The units are mg KOH per gram  
 26 sample.

27

28 The term "succinic group" refers to a group having the formula

29

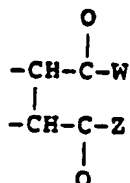
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01 wherein W and Z are independently selected from the group  
02 consisting of -OH, -Cl, -O- lower alkyl or taken together  
03 are -O- to form a succinic anhydride group. The term "-O-  
04 lower alkyl" is meant to include alkoxy of 1 to 6 carbon  
05 atoms.

06

07 The term "degree of polymerization" expresses the length of  
08 a linear polymer and refers to the number of repeating  
09 (monomeric) units in the chain. The average molecular  
10 weight of a polymer is the product of the degree of polymer-  
11 ization and the average molecular weight of the repeating  
12 unit (monomer). Accordingly, the average degree of poly-  
13 merization is calculated by dividing the average molecular  
14 weight of the polymer by the average molecular weight of the  
15 repeating unit.

16

17 The term "polysuccinimide" refers to the reaction product of  
18 a copolymer made by the present process with polyamine.

19

20

21

## DETAILED DESCRIPTION OF THE INVENTION

22

23

### A. COPOLYMER

24

25 The copolymers made by the present process are prepared by  
26 reacting a high molecular weight olefin wherein at least  
27 about 20% of the total olefin composition comprises the  
28 alkylvinylidene isomer and an unsaturated acidic reactant in  
29 the presence of a free radical initiator and a solvent com-  
30 prising the reaction product of an unsaturated acidic  
31 reactant and a high molecular weight olefin. Preferably,  
32 the solvent comprises (a) an oligomeric copolymer of an  
33 unsaturated acidic reactant and a high molecular weight  
34 olefin or (b) a monomeric adduct of an unsaturated acidic

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01 reactant and a high molecular weight olefin in at least a  
02 one to one mole ratio of acidic reactant to olefin, or a  
03 mixture thereof. Suitable high molecular weight olefins  
04 have a sufficient number of carbon atoms so that the  
05 resulting copolymer is soluble in lubricating oil and thus  
06 have on the order of about 32 carbon atoms or more. Pre-  
07 ferred high molecular weight olefins are polyisobutenes and  
08 polypropylenes. Especially preferred are polyisobutenes,  
09 particularly preferred are those having a molecular weight  
10 of about 500 to about 5000, more preferably about 900 to  
11 about 2500. Preferred unsaturated acidic reactants include  
12 maleic anhydride.

13

14 Since the high molecular weight olefins used in the process  
15 of the present invention are generally mixtures of indi-  
16 vidual molecules of different molecular weights, individual  
17 copolymer molecules resulting will generally contain a mix-  
18 ture of high molecular weight polyalkyl groups of varying  
19 molecular weight. Also, mixtures of copolymer molecules  
20 having different degrees of polymerization will be produced.

21

22 The copolymers made by the process of the present invention  
23 have an average degree of polymerization of 1 or greater,  
24 preferably from about 1.1 to about 20, and more preferably  
25 from about 1.5 to about 10.

26

27 In accordance with the process of the present invention, the  
28 desired copolymer products are prepared by reacting a "reac-  
29 tive" high molecular weight olefin in which a high propor-  
30 tion of unsaturation, at least about 20%, is in the  
31 alkylvinylidene configuration, e.g.,

32

33

34

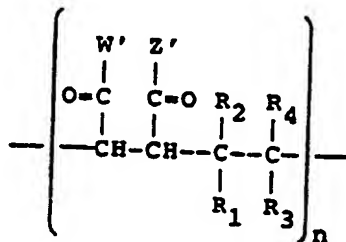
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wherein R and R<sub>V</sub> are as previously defined in conjunction with Formula III, with an unsaturated acidic reactant in the presence of a free radical initiator and an oligomeric or monomeric solvent as described above. The product copolymer has alternating polyalkylene and succinic groups and has an average degree of polymerization of 1 or greater.

The copolymers prepared by the instant process have the general formula:

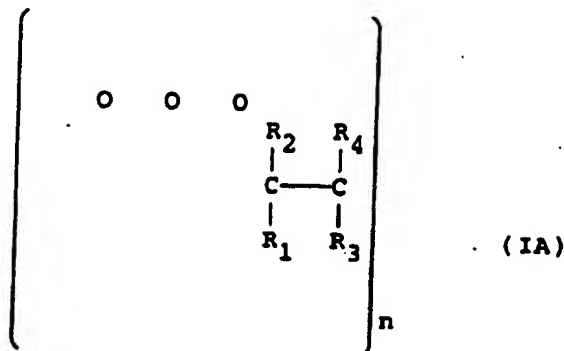


wherein W' and Z' are independently selected from the group consisting of -OH, -O- lower alkyl or taken together are -O- to form a succinic anhydride group, n is one or greater; and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are selected from hydrogen, lower alkyl of 1 to 6 carbon atoms, and high molecular weight polyalkyl wherein either R<sub>1</sub> and R<sub>2</sub> are hydrogen and one of R<sub>3</sub> and R<sub>4</sub> is lower alkyl and the other is high molecular weight polyalkyl, or R<sub>3</sub> and R<sub>4</sub> are hydrogen and one of R<sub>1</sub> and R<sub>2</sub> is lower alkyl and the other is high molecular weight polyalkyl.

In a preferred embodiment, when maleic anhydride is used as the unsaturated acidic reactant, the reaction produces copolymers predominately of the following formula:

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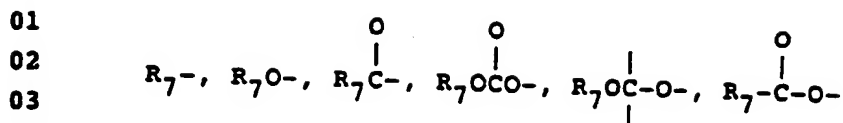
wherein n is about 1 to about 100, preferably about 2 to about 20, more preferably 2 to 10, and  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are selected from hydrogen, lower alkyl of about 1 to 6 carbon atoms and higher molecular weight polyalkyl, wherein either  $\text{R}_1$  and  $\text{R}_2$  are hydrogen and one of  $\text{R}_3$  and  $\text{R}_4$  is lower alkyl and the other is high molecular weight polyalkyl or  $\text{R}_3$  and  $\text{R}_4$  are hydrogen and one of  $\text{R}_1$  and  $\text{R}_2$  is lower alkyl and the other is high molecular weight polyalkyl.

Preferably, the high molecular weight polyalkyl group has at least about 30 carbon atoms, preferably at least about 50 carbon atoms. Preferred high molecular weight polyalkyl groups include polyisobutyl groups. Preferred polyisobutyl groups include those having average molecular weights of about 500 to about 5000, more preferably from about 900 to about 2500. Preferred lower alkyl groups include methyl and ethyl; especially preferred lower alkyl groups include methyl.

Generally, such copolymers contain an initiator group, I, and a terminator group, T, as a result of the reaction with the free radical initiator used in the polymerization reaction. In such a case, the initiator and terminator groups may be

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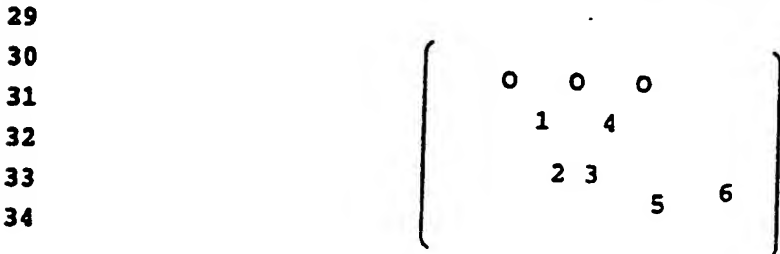
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05 where  $R_7$  is hydrogen, alkyl, aryl, alkaryl, cycloalkyl,  
 06 alkoxy, cycloalkoxy, acyl, alkenyl, cycloalkenyl, alkynyl,  
 07 or alkyl, aryl or alkaryl optionally substituted with 1 to 4  
 08 substituents independently selected from nitrile, keto,  
 09 halogen, nitro, alkyl, aryl, and the like. Alternatively,  
 10 the initiator group and/or terminator group may be derived  
 11 from the reaction product of the initiator with another  
 12 material, such as solvent.

13  
 14 The copolymers prepared by the present process differ from  
 15 the PIBSAs prepared by the thermal process in that the  
 16 thermal process products contain a double bond and a singly  
 17 substituted succinic anhydride group, that is, a monomeric  
 18 one to one adduct. The copolymers prepared by the present  
 19 process differ from the PIBSAs prepared by the chlorination  
 20 process, since those products contain a double bond, a ring  
 21 other than a succinic anhydride ring, or one or more  
 22 chlorine atoms.

23  
 24 The copolymers prepared by the present process contain no  
 25 double bonds, rings other than succinic anhydride rings, or  
 26 chlorine atoms. In addition, the succinic anhydride groups  
 27 are doubly substituted (i.e., have two substituents, one of  
 28 which may be hydrogen) at the 2- and 3-positions, that is:



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01           A(1) High Molecular Weight Polyalkylene Group  
02

03   The high molecular weight polyalkyl group is derived from a  
04   high molecular weight olefin. The high molecular weight  
05   olefins used in the preparation of the instant copolymers  
06   are of sufficiently long chain length so that the resulting  
07   composition is soluble in and compatible with mineral oils,  
08   fuels and the like; and the alkylvinylidene isomer of the  
09   high molecular weight olefin comprises at least about 20% of  
10   the total olefin composition.

11  
12   Such high molecular weight olefins are generally mixtures of  
13   molecules having different molecular weights and can have at  
14   least one branch per 6 carbon atoms along the chain, pre-  
15   ferably at least one branch per 4 carbon atoms along the  
16   chain, and particularly preferred that there be about one  
17   branch per 2 carbon atoms along the chain. These branched  
18   chain olefins may conveniently comprise polyalkenes prepared  
19   by the polymerization of olefins of from 3 to 6 carbon  
20   atoms, and preferably from olefins of from 3 to 4 carbon  
21   atoms, and more preferably from propylene or isobutylene.  
22   The addition-polymerizable olefins employed are normally  
23   1-olefins. The branch may be of from 1 to 4 carbon atoms,  
24   more usually of from 1 to 2 carbon atoms and preferably  
25   methyl.

26  
27   The preferred alkylvinylidene isomer comprises a methyl- or  
28   ethylvinylidene isomer, more preferably the methylvinylidene  
29   isomer.

30  
31   The especially preferred high molecular weight olefins used  
32   to prepare the instant copolymers are polyisobutenes which  
33   comprise at least about 20% of the more reactive methyl-  
34   vinylidene isomer, preferably at least 50% and more

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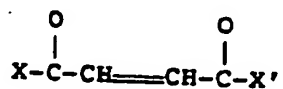
01 preferably at least 70%. Suitable polyisobutenes include  
 02 those prepared using  $\text{BF}_3$  catalysis. The preparation of such  
 03 polyisobutenes in which the methylvinylidene isomer com-  
 04 prises a high percentage of the total composition is  
 05 described in U.S. Patents Nos. 4,152,499 and 4,605,808.  
 06

07 Polyisobutenes produced by conventional  $\text{AlCl}_3$  catalysis when  
 08 reacted with unsaturated acidic reactants, such as maleic  
 09 anhydride, in the presence of a free radical initiator, pro-  
 10 duce products similar to thermal PIBSA in molecular weight  
 11 and thus do not produce a copolymeric product.  
 12

13 Preferred are polyisobutenes having average molecular  
 14 weights of about 500 to about 5000. Especially preferred  
 15 are those having average molecular weights of about 900 to  
 16 about 2500.  
 17

#### 18 A(2) Unsaturated Acidic Reactant

19  
 20 The unsaturated acidic reactant used in the preparation of  
 21 the instant copolymers comprises a maleic or fumaric  
 22 reactant of the general formula:  
 23



24  
 25  
 26  
 27 wherein X and X' are the same or different, provided that at  
 28 least one of X and X' is a group that is capable of reacting  
 29 to esterify alcohols, form amides or amine salts with ammo-  
 30 nia or amines, form metal salts with reactive metals or  
 31 basically reacting metal compounds and otherwise function to  
 32 acylate. Typically, X and/or X' is -OH, -O-hydrocarbyl,  
 33  $-\text{OM}^+$  where  $\text{M}^+$  represents one equivalent of a metal, ammonium  
 34 or amine cation,  $-\text{NH}_2$ , -Cl, -Br, and taken together X and X'

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01 can be -O- so as to form an anhydride. Preferably, X and X'  
02 are such that both carboxylic functions can enter into  
03 acylation reactions. Preferred are acidic reactants where X  
04 and X' are each independently selected from the group con-  
05 sisting of -OH, -Cl, -O- lower alkyl and when taken  
06 together, X and X' are -O-. Maleic anhydride is the pre-  
07 ferred acidic reactant. Other suitable acidic reactants  
08 include electron-deficient olefins such as monophenyl maleic  
09 anhydride; monomethyl, dimethyl, monochloro, monobromo,  
10 monofluoro, dichloro and difluoro maleic anhydride; N-phenyl  
11 maleimide and other substituted maleimides; isomaleimides;  
12 fumaric acid, maleic acid, alkyl hydrogen maleates and  
13 fumarates, dialkyl fumarates and maleates, fumaronilic acids  
14 and maleanic acids; and maleonitrile, and fumaronitrile.  
15  
16 Preferred unsaturated acidic reactants include maleic  
17 anhydride, and maleic acid. The particularly preferred  
18 acidic reactant is maleic anhydride.

19  
20 A(3) General Preparation of Copolymer  
21

22 As noted above, the copolymers made by the process of the  
23 invention are prepared by reacting a reactive high molecular  
24 weight olefin and an unsaturated acidic reactant in the  
25 presence of a free radical initiator and a specific solvent,  
26 as described herein.

27  
28 As discussed above, in U.S. Patent Application Serial  
29 No. 251,613 it is taught that the reaction of high molecular  
30 weight olefin and unsaturated acidic reactant in the  
31 presence of a free radical initiator may be conducted neat  
32 or with a solvent, such as a saturated or aromatic hydro-  
33 carbon, a ketone or a liquid saturated aliphatic  
34 dihalogenated hydrocarbon.

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01 It has now been found that when this reaction is carried out  
02 neat, that is, in the absence of any solvent, a significant  
03 amount of resin is formed, presumably from polymerization of  
04 the unsaturated acidic reactant.

05

06 This problem can be somewhat avoided by employing a  
07 halogenated hydrocarbon solvent, but the use of such sol-  
08 vents also has certain drawbacks. Halogenated hydrocarbon  
09 solvents are both expensive and environmentally undesirable.  
10 Moreover, they impede the recycling of lubricating oils  
11 because of the residual halogen content.

12

13 It has now been discovered that oligomeric copolymers of  
14 high molecular weight olefins and unsaturated acidic reac-  
15 tants can be prepared in improved yields by employing a  
16 solvent which comprises the reaction product of an  
17 unsaturated acidic reactant and a high molecular weight  
18 olefin. Preferably, the solvent comprises either (a) an  
19 oligomeric copolymer of an unsaturated acidic reactant and a  
20 high molecular weight olefin or (b) a monomeric adduct of an  
21 unsaturated acidic reactant and a high molecular weight  
22 olefin in at least a one-to-one mole ratio of acidic  
23 reactant to olefin. Mixtures of (a) and (b) may also be  
24 employed as the solvent.

25

26 For use as a solvent, the oligomeric copolymer of  
27 unsaturated acidic reactant and high molecular weight olefin  
28 can be conveniently obtained by retaining a portion of the  
29 oligomeric copolymer product from a previous run. Alterna-  
30 tively, the solvent may be a monomeric adduct of an  
31 unsaturated acidic reactant and a high molecular weight  
32 olefin in at least a 1:1 ratio of acid to olefin, which can  
33 be readily prepared via the known "thermal process" or the  
34 known "chlorination process", as described above. For use

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01 in preparing the monomeric adduct, the high molecular weight  
02 olefin may contain less than 20% of the alkylvinylidene  
03 isomer.

04

05 Preferred solvents include the oligomeric copolymer product  
06 of maleic anhydride and polyisobutene, that is, "polyPIBSA",  
07 as defined above, and the monomeric adduct of maleic  
08 anhydride and polyisobutene, namely, polyisobutenyl succinic  
09 anhydride or "PIBSA". A particularly preferred solvent is  
10 polyPIBSA.

11

12 The "thermal" PIBSA described above is well known in the  
13 art. One method of preparing thermal PIBSA is disclosed in  
14 U.S. Patent No. 3,361,673, the disclosure of which is  
15 incorporated herein by reference for its teachings on  
16 preparing thermal PIBSA. The "chlorination process" PIBSA  
17 described above is also well known in the art. One method  
18 of preparing chlorination process PIBSA is disclosed in  
19 U.S. Patent No. 3,172,892, the disclosure of which is  
20 incorporated herein by reference for its teachings in  
21 preparing chlorination process PIBSA.

22

23 The amount of solvent employed should be such that it can  
24 dissolve the acidic reactant and the high molecular weight  
25 olefin, in addition to the resulting copolymers. The volume  
26 ratio of solvent to high molecular weight olefin is suitably  
27 between 1:1 and 100:1, and is preferably between 1.5:1 and  
28 4:1.

29

30 The reaction may be conducted at a temperature in the range  
31 of about 90°C to about 210°C, and preferably from about  
32 130°C to about 150°C. Reaction at lower temperatures works  
33 to a point, but the reaction solution generally becomes  
34 viscous and therefore requires added heat to obtain

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01 satisfactory reaction. Although not wishing to be bound by  
02 any theory, it is believed that there is a so-called "cage-  
03 effect", wherein the free radical initiator is trapped in  
04 the solvent/reaction mixture and therefore cannot  
05 effectively initiate the polymerization reaction.

06  
07 Although it has been observed that reaction may be slow or  
08 incomplete below the preferred temperature range of about  
09 130°C to 150°C, it is envisioned that stepping the reaction  
10 temperature up in increments from a minimum of about 90°C  
11 could provide advantageous results. The highest temperature  
12 of these incremental temperature steps is preferably above  
13 about 140°C when complete reaction is desired.

14  
15 In general, the copolymerization process of the present  
16 invention can be initiated by any free radical initiator.  
17 Such initiators are well known in the art. However, the  
18 choice of free radical initiator may be influenced by the  
19 reaction temperature employed.

20  
21 The preferred free-radical initiators are the peroxide-type  
22 polymerization initiators and the azo-type polymerization  
23 initiators. Radiation can also be used to initiate the  
24 reaction, if desired.

25  
26 The peroxide-type free-radical initiator can be organic or  
27 inorganic, the organic having the general formula:  $R_3OOR_3'$   
28 where  $R_3$  is any organic radical and  $R_3'$  is selected from the  
29 group consisting of hydrogen and any organic radical. Both  
30  $R_3$  and  $R_3'$  can be organic radicals, preferably hydrocarbon,  
31 aroyl, and acyl radicals, carrying, if desired, substituents  
32 such as halogens, etc. Preferred peroxides include di-tert-  
33 butyl peroxide, tert-butyl peroxybenzoate, and dicumyl  
34 peroxide.

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01 Examples of other suitable peroxides, which in no way are  
02 limiting, include benzoyl peroxide; lauroyl peroxide; other  
03 tertiary butyl peroxides; 2,4-dichlorobenzoyl peroxide;  
04 tertiary butyl hydroperoxide; cumene hydroperoxide; diacetyl  
05 peroxide; acetyl hydroperoxide; diethylperoxycarbonate;  
06 tertiary butyl perbenzoate; and the like.

07

08 The azo-type compounds, typified by alpha, alpha'-azo-bisiso-  
09 butyronitrile, are also well-known free-radical promoting  
10 materials. These azo compounds can be defined as those  
11 having present in the molecule group -N=N wherein the  
12 balances are satisfied by organic radicals, at least one of  
13 which is preferably attached to a tertiary carbon. Other  
14 suitable azo compounds include, but are not limited to,  
15 p-bromobenzenediazonium fluoborate; p-tolyldiazoaminoben-  
16 zene; p-bromobenzenediazonium hydroxide; azomethane and  
17 phenyldiazonium halides. A suitable list of azo-type com-  
18 pounds can be found in U.S. Patent No. 2,551,813, issued  
19 May 8, 1951 to Paul Pinkney.

20

21 The amount of initiator to employ, exclusive of radiation,  
22 of course, depends to a large extent on the particular  
23 initiator chose, the high molecular olefin used and the  
24 reaction conditions. The initiator must, of course, be  
25 soluble in the reaction medium. The usual concentrations of  
26 initiator are between 0.001:1 and 0.2:1 moles of initiator  
27 per mole of acidic reactant, with preferred amounts between  
28 0.005:1 and 0.10:1.

29

30 In carrying out the process of the invention, a single free  
31 radical initiator or a mixture of free radical initiators  
32 may be employed. The initiator may also be added over time.  
33 For example, it may be desirable to add an initiator having  
34 a low decomposition temperature as the mixture is warming to

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01 intended to apply equally well to the copolymer reaction  
02 product of any of the unsaturated acidic reactants and high  
03 molecular weight olefins described herein.

04

05 The reaction can be run either batchwise or continuously.  
06 The reaction temperature range is about 90°C to 210°C and  
07 preferably about 130°C to 150°C. The reactor temperature  
08 effects the molecular weight distribution, and this can  
09 influence the ratio of maleic anhydride to polybutene that  
10 is fed to the reactor. Theoretically the maleic anhydride  
11 charge can range from 1 to 2 moles of maleic anhydride per  
12 mole of methyl vinylidene isomer of PIB. Typically, the  
13 free radical initiator is charged at 0.1 moles initiator per  
14 1.0 moles maleic anhydride, although this can vary. The  
15 reaction can be carried out at atmospheric pressure,  
16 although at the higher temperature range it may be desirable  
17 to pressurize the reactor slightly (i.e., 10 psig) to  
18 suppress the loss of maleic anhydride to the vapor phase.  
19 Neutral oil can be used to reduce the viscosity of the  
20 mixture, but this can be deleterious to the reaction rate  
21 and productivity of the reactor.

22

23 If the reaction is run batchwise, PIB and polyPIBSA from a  
24 previous run are charged to the reactor. Thermal process  
25 PIBSA or chlorination process PIBSA may also be used in lieu  
26 of or in addition to polyPIBSA. The ratio of PIB to  
27 polyPIBSA should be such as to assure complete solubility of  
28 maleic anhydride in the mixture at reaction conditions. If  
29 polyPIBSA is not added at a sufficient level so as to  
30 maintain total maleic anhydride solubility, the rate of  
31 reaction can be negatively affected, and the formation of  
32 resin may be likely. To maximize reactor productivity, the  
33 minimum amount of polyPIBSA that is necessary to maintain  
34 total solubility of the maleic anhydride charge should be

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01 used. The reactor is stirred and heated to the desired  
02 reaction temperature, and the maleic anhydride and free  
03 radical initiator are added at the appropriate time/times  
04 during this step. Reaction times will vary with temper-  
05 ature, concentration of reactants, and types of free radical  
06 initiators. Reactions performed at 140°C, for example, were  
07 nearly complete according to  $^{13}\text{C}$  NMR in roughly two hours.  
08 When the reaction is complete, removal of any unreacted  
09 maleic anhydride can be accomplished by increasing the  
10 reactor temperature to 150°C to 250°C, preferably 180°C to  
11 200°C, while applying sufficient vacuum. This procedure  
12 also tends to decompose any remaining free radical initia-  
13 tor. Another method for removal of unreacted maleic  
14 anhydride is the addition of a solvent (e.g., hexane) which  
15 solubilizes the polyPIBSA and precipitates the maleic  
16 anhydride. The mixture then is filtered to remove the  
17 maleic anhydride followed by stripping to remove the  
18 solvent.

19  
20 If the reaction is run continuously, a continuous stirred  
21 tank reactor (CSTR) or series of such reactors can be used.  
22 Reaction conditions should be selected to maintain the bulk  
23 concentration of polyPIBSA at a sufficient level to maintain  
24 maleic anhydride solubility in the reactor or series of  
25 reactors. A continuous reactor is thought to be particu-  
26 larly advantageous for reactions carried out at the lower  
27 temperature range. As the temperature is reduced, the  
28 maleic anhydride solubility in the polyPIBSA/polybutene  
29 mixture decreases and this necessitates that the polyPIBSA  
30 concentration be increased or the maleic anhydride concen-  
31 tration be decreased so that total solubility of the maleic  
32 anhydride is maintained. In a batch process an increase in  
33 the initial charge of polyPIBSA can result in a decrease in  
34 reactor productivity. Likewise, decreasing the maleic

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01 anhydride charge or extending the addition of maleic  
02 anhydride over a time period can decrease reactor produc-  
03 tivity. On the other hand, in a CSTR at steady state con-  
04 ditions the polyPIBSA concentration in the bulk mixture is  
05 not only constant, but it is essentially the same the  
06 product exiting the reactor. Therefore, the polyPIBSA  
07 concentration in a CSTR is at a maximum (equal to the  
08 polyPIBSA product for a single stage CSTR) when compared to  
09 a simple batch process where the all polybutene is charged  
10 at the beginning of the reaction and the polyPIBSA concen-  
11 tration is at a minimum.

12

13 For the continuous reactor, the temperature can range from  
14 90°C to 210°C and preferably from 130°C to 150°C. PIB,  
15 maleic anhydride, and free-radical initiator can be fed  
16 continuously at appropriate rates so as to maintain a  
17 certain level of conversion of the reactants to polyPIBSA.  
18 It is envisioned that the product stream from the reactor  
19 then is heated to a temperature in the range of 150°C to  
20 250°C and preferably in the range from 180°C to 200°C to  
21 strip off any unreacted maleic anhydride and to decompose  
22 any remaining free-radical initiator. Vacuum can also be  
23 sued to facilitate removal of the unreacted maleic  
24 anhydride. It is envisioned that a wiped film evaporator or  
25 similar types of equipment may be suitable for this type of  
26 operation.

27

28 In one envisioned embodiment, the reaction product of an  
29 unsaturated acidic reactant and a high molecular weight,  
30 high vinylidene-containing olefin is further reacted  
31 thermally. In this embodiment, any unreacted olefin,  
32 generally the more hindered olefins, i.e., the non-vinyl-  
33 idene, that do not react readily with the unsaturated acidic  
34 reactant under free radical conditions are reacted with

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01 unsaturated acidic reactant under thermal conditions, i.e.,  
02 at temperatures of about 180° to 280°C. These conditions  
03 are similar to those used for preparing thermal PIBSA.  
04

05 The reaction solvent, as noted above, must be one which  
06 dissolves both the acidic reactant and the high molecular  
07 weight olefin. It is necessary to dissolve the acidic  
08 reactant and high molecular weight olefin so as to bring  
09 them into intimate contact in the solution polymerization  
10 reaction. It has been found that the solvent must also be  
11 one in which the resultant copolymers are soluble.  
12

13 It has been found that a small amount of haze or resin,  
14 typically less than one gram per liter, is observed at the  
15 end of reaction. Accordingly, the reaction mixture is  
16 typically filtered hot to remove this haze or resin.  
17

18 In general, after the reaction is deemed complete, for  
19 example, by NMR analysis, the reaction mixture is heated to  
20 decompose any residual initiator. For a di(t<sub>i</sub>-butyl)  
21 peroxide initiator, this temperature is typically about  
22 160°C.  
23

24 The isolated copolymer may then be reacted with a polyamine  
25 to form a polymeric succinimide. The preparation and  
26 characterization of such polysuccinimides and their treat-  
27 ment with other agents to give other dispersant compositions  
28 is described herein.  
29

#### 30 A(4) Preferred Copolymers

31

32 Preferred copolymers prepared by the present process include  
33 those where an unsaturated acidic reactant, most preferably  
34 maleic anhydride, is copolymerized with a "reactive"

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01 polyisobutene, in which at least about 50 percent or more of  
02 the polyisobutene comprises the alkylvinylidene, more  
03 preferably, the methylvinylidene, isomer, to give a  
04 "polyPIBSA".

05

06 Preferred are polyPIBSAs wherein the polyisobutyl group has  
07 an average molecular weight of about 500 to about 5000, more  
08 preferably from about 950 to about 2500. Preferred are  
09 polyPIBSAs having an average degree of polymerization of  
10 about 1.1 to about 20, more preferably from about 1.5 to  
11 about 10.

12

13

#### B. POLYSUCCINIMIDES

14

15 As noted above, polyamino polysuccinimides may be convenien-  
16 tly prepared by reacting a copolymer made by the present  
17 process with a polyamine. Polysuccinimides which may be  
18 prepared include monopolsuccinimides (where a polyamine  
19 component reacts with one succinic group), bis-polysuccini-  
20 mides (where a polyamine component reacts with a succinic  
21 group from each of two copolymer molecules), higher succi-  
22 nimides (where a polyamine component reacts with a succinic  
23 group from each of more than 2 copolymer molecules) or  
24 mixtures thereof. The polysuccinimide(s) produced may  
25 depend on the charge mole ratio of polyamine to succinic  
26 groups in the copolymer molecule and the particular poly-  
27 amine used. Using a charge mole ratio of polyamine to  
28 succinic groups in copolymer of about 1.0, predominately  
29 monopolsuccinimide is obtained. Charge mole ratios of  
30 polyamine to succinic group in copolymer of about 1:2 may  
31 produce predominately bis-polysuccinimide. Higher poly-  
32 succinimides may be produced if there is branching in the  
33 polyamine so that it may react with a succinic group from  
34 each of greater than 2 copolymer molecules.

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01 The copolymers made by the present process, including  
02 preferred copolymers such as polyPIBSA, may be post-treated  
03 with a wide variety of other post-treating reagents. U.S.  
04 Patent No. 4,234,435, the disclosure of which is incorpo-  
05 rated herein by reference, discloses reacting succinic  
06 acylating agents with a variety of reagents to give post-  
07 treated carboxylic acid derivative compositions which are  
08 useful in lubricating oil compositions.

09

10

#### C. LUBRICATING OIL COMPOSITIONS

11

12 The copolymers, polysuccinimides and modified polysuccini-  
13 mides described herein are useful as detergent and disper-  
14 sant additives when employed in lubricating oils. When  
15 employed in this manner, these additives are usually present  
16 in from 0.2 to 10 percent by weight to the total composition  
17 and preferably at about 0.5 to 8 percent by weight and more  
18 preferably at about 1 to about 6 percent by weight. The  
19 lubricating oil used with these additive compositions may be  
20 mineral oil or synthetic oils of lubricating viscosity and  
21 preferably suitable for use in the crankcase of an internal  
22 combustion engine. Crankcase lubricating oils ordinarily  
23 have a viscosity of about 1300 CSt 0°F to 22.7 CSt at 210°F  
24 (99°C). The lubricating oils may be derived from synthetic  
25 or natural sources. Mineral oil for use as the base oil in  
26 this invention includes paraffinic, naphthenic and other  
27 oils that are ordinarily used in lubricating oil composi-  
28 tions. Synthetic oils include both hydrocarbon synthetic  
29 oils and synthetic esters. Useful synthetic hydrocarbon  
30 oils include liquid polymers of alpha olefins having the  
31 proper viscosity. Especially useful are the hydrogenated  
32 liquid oligomers of C<sub>6</sub> to C<sub>12</sub> alpha olefins such as 1-decene  
33 trimer. Likewise, alkyl benzenes of proper viscosity, such  
34 as didodecyl benzene, can be used.

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01 Blends of hydrocarbon oils with synthetic oils are also  
02 useful. For example, blends of 10 to 25 weight percent  
03 hydrogenated 1-decene trimer with 75 to 90 weight percent  
04 150 SUS (100°F) mineral oil gives an excellent lubricating  
05 oil base.

06

07 Lubricating oil concentrates are also envisioned. These  
08 concentrates usually include from about 90 to 10 weight  
09 percent, preferably from about 90 to about 50 weight  
10 percent, of an oil of lubricating viscosity and from about  
11 10 to 90 weight percent, preferably from about 10 to about  
12 50 weight percent, of an additive described herein. Typi-  
13 cally, the concentrates contain sufficient diluent to make  
14 them easy to handle during shipping and storage. Suitable  
15 diluents for the concentrates include any inert diluent,  
16 preferably an oil of lubricating viscosity, so that the  
17 concentrate may be readily mixed with lubricating oils to  
18 prepare lubricating oil compositions. Suitable lubricating  
19 oils which can be used as diluents typically have viscosi-  
20 ties in the range from about 35 to about 500 Saybolt  
21 Universal Seconds (SUS) at 100°F (38°C), although an oil of  
22 lubricating viscosity may be used.

23

24 Other additives which may be present in the formulation  
25 include rust inhibitors, foam inhibitors, corrosion  
26 inhibitors, metal deactivators, pour point depressants,  
27 antioxidants, and a variety of other well-known additives.

28

29 It is also contemplated that the additives described herein  
30 may be employed as dispersants and detergents in hydraulic  
31 fluids, marine crankcase lubricants and the like. When so  
32 employed, the additive is added at from about 0.1 to 10  
33 percent by weight to the oil. Preferably, at from 0.5 to 8  
34 weight percent.

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D. FUEL COMPOSITIONS

01  
02  
03 When used in fuels, the proper concentration of the additive  
04 necessary in order to achieve the desired detergency is  
05 dependent upon a variety of factors including the type of  
06 fuel used, the presence of other detergents or dispersants  
07 or other additives, etc. Generally, however, the range of  
08 concentration of the additive in the base fuel is 10 to  
09 10,000 weight parts per million, preferably from 30 to 5000  
10 parts per million of the additive per part of base fuel. If  
11 other detergents are present, a lesser amount of the addi-  
12 tive may be used. The additives described herein may be  
13 formulated as a fuel concentrate, using an inert stable  
14 oleophilic organic solvent boiling in the range of about  
15 150° to 400°F. Preferably, an aliphatic or an aromatic  
16 hydrocarbon solvent is used, such a benzene, toluene, xylene  
17 or higher-boiling aromatics or aromatic thinners. Aliphatic  
18 alcohols of about 3 to 8 carbon atoms, such as isopropanol,  
19 isobutylcarbinol, n-butanol and the like, in combination  
20 with hydrocarbon solvents are also suitable for use with the  
21 fuel additive. In the fuel concentrate, the amount of the  
22 additive will be ordinarily at least 5 percent by weight and  
23 generally not exceed 70 percent by weight, preferably from 5  
24 to 50 and more preferably from 10 to 25 weight percent.  
25  
26 The following examples are offered to specifically illus-  
27 trate this invention. These examples and illustrations are  
28 not to be construed in any way limiting the scope of this  
29 invention.

30  
31  
32  
33  
34

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EXAMPLESExample 1 (Comparative)Preparation of Polyisobutyl-24 PolyPIBSA

To a 12-liter, 3-neck flask equipped with an overhead stirrer, thermometer, condenser, and heating mantle under nitrogen atmosphere was added 5,000 grams (5.265 mole) of polyisobutene of about 950 molecular weight having the trade name ULTRAVIS-10 obtained from BP Chemicals wherein the methylvinylidene isomer comprised about 70% of the total composition, 1547.1 grams (15.79 mole) maleic anhydride, and 2,500 ml chloroform. The mixture was heated to reflux, and to this was added 67.21 grams (0.41 mole) 22'-azobis (2-methyl-propionitrile) ("AIBN"). The mixture was refluxed for two hours at which time an additional 67.21 grams of AIBN was added. This was followed by another two hours of reflux and a third charge (66.58 grams) of AIBN. A total of 201 grams (1.2 mole) of AIBN was added. The reaction mixture was refluxed a total of 20 hours, and then allowed to cool. Two layers formed. The lower phase which contained mostly chloroform and unreacted maleic anhydride was discarded. The upper layer which contained mainly product and unreacted polyisobutene was separated. Solvent and maleic anhydride were removed in vacuo. A total of 4,360 grams of product having a saponification number of 40.4 was recovered.

Example 2 (Comparative)Preparation of Polyisobutyl-24 PolyPIBSA

To a 1-liter 3-neck flask equipped with a thermometer, overhead stirrer, nitrogen inlet and water condenser, was added 165.02 grams (0.174 mole) polyisobutylene (ULTRAVIS-10 from

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01 BP Chemicals) and 105 ml dichloroethane, then 16.4 grams  
02 (0.167 mole) maleic anhydride were added. The resulting  
03 mixture was heated to about 45°C, and 3.3 grams (0.017 mole)  
04 tert-butylperbenzoate was added. The resulting mixture was  
05 heated to reflux (83°C). The reaction mixture was heated  
06 (with stirring) for a total of 30 hours. The reaction mix-  
07 ture was allowed to cool. The solvent was removed in vacuo.  
08 Unreacted maleic anhydride was removed by heating the resi-  
09 due to 150°C at 0.1 mm Hg vacuum. A total of 176.0 grams  
10 product was obtained, which had an average molecular weight  
11 of about 5000. The conversion was about 60%. The  
12 saponification number was 73.3.

13

14 Examples 3 to 15 and Examples 1C to 5C (Comparative)

15

16 Table I tabulates additional preparations following the  
17 basic synthetic procedure outlined in Examples 1 and 2.  
18 Table I lists the reactants, reaction temperature, time and  
19 solvent, and free radical initiator used.

20

21 Example 12 was prepared using polyisobutene of about 1300  
22 molecular weight having the trade name ULTRAVIS-30 obtained  
23 from BP chemicals wherein the methylvinylidene isomer  
24 comprised about 70% of the total composition.

25

26 Comparison Examples 1C to 5C were prepared using a polyiso-  
27 butylene of about 950 molecular weight prepared with  
28  $\text{AlCl}_3$  catalysis having the trade name Parapol 950 obtained  
29 from Exxon Chemical.

30

31

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TABLE I

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator* (g)	Temp °C	Time Hrs.
2	Ultravis-10 (165.09)	16.4	Dichloroethane (105)	TBPP (3.3)	83	30
3	Ultravis-10 (384.6)	119	Toluene (250)	AIBN (15.5)	110	6
4	Ultravis-10 (330)	32.3	Chlorobenzene (210)	DTBP (5.8)	138	30
5	Ultravis-10 (5000)	1547	Dichloroethane (2500)	AIBN (200)	83	13
6	Ultravis-10 (384.6)	119	Chloroform (250)	AIBN (15.5)	74	24
7	Ultravis-10 (384.6)	119	Methylene Chloride (250)	AIBN (15.5)	40	94
8	Ultravis-10 (330)	32.3	Toluene (210)	DTBP (5.8)	110	30
9	Ultravis-10 (330)	32.3	Xylene (210)	DTBP (5.8)	144	39
10	Ultravis-10 (330)	32.3	Xylene (210)	DTBP (5.8)	114	4
11	Ultravis-10 (330)	32.3	Toluene (210)	DTBP (5.8)	110	4
12	Ultravis-30 (217.1)	16.4	Dichloroethane (105)	TBPP (3.3)	83-184	26
13	Ultravis-10 (3350)	328.3	Chlorobenzene (1600)	DTBP (42.6)	138	28

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TABLE I (Cont'd)

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator* (g)	Temp °C	Time Hrs.
14	Ultravis-10 (5000)	515.8	Chloroform (3000)	TBFB (102.8)	72	54
15	Ultravis-10 (10,000)	1031	Chloroform (6000)	TBFB (205.6) then	72 140	48 2
1C	Parapol 950 (384.6)	119	Toluene (250)	AIBN (15.5)	110	6
2C	Parapol 950 (76.4)	23.8	Dichloroethane (50)	AIBN (2.33)	83	4
3C	Parapol 950 (330)	32.3	Toluene (210)	DTBP (5.8)	110	30
4C	Parapol 950 (330)	32.3	Xylene (210)	DTBP (5.8)	114	30
5C	Parapol 950 (330)	32.3	Chlorobenzene (210)	DTBP (5.8)	138	30

\* AIBN = 2,2'-azobis (2-methyl-propionitrile); DTBP = di-tert-butyl peroxide; TBFB = tertbutyl peroxybenzoate

\*\* Molecular weight 1300

Example 16

A 500-ml, 3-necked flask was charged with 100g of a polyPIBSA/polybutene mixture (prepared according to the method of Example 5) which comprised about 38 weight percent polyPIBSA and about 62 weight percent (0.0653 mol) unreacted polyisobutene (of which about 68 weight percent (0.0444 mol) comprised the methylvinylidene isomer). The mixture was heated to 70°C. Then, 8g (0.0816 mol) maleic anhydride and 1.7g (0.0116 mol) di-tert-butyl peroxide were added to the

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01 mixture. The mixture was stirred and heated to 150°C for  
02 5 hours. After allowing the mixture to cool, 150 ml hexane  
03 was added to precipitate unreacted maleic anhydride which  
04 was then removed by filtration. The hexane was removed by  
05 stripping for 4 hours at 36 mm Hg (abs) at 90°C. The  
06 filtered product had an unreacted maleic anhydride content  
07 of 0.08 weight percent, as determined by gas chromatography.  
08 The saponification number of the final product was deter-  
09 mined to be 84 mg KOH/g sample. The amount of unreacted  
10 polybutene was determined to be 28.2% by column  
11 chromatography.

12

13

Example 17A

14

15 A 22-liter, 3-necked flask was charged with 3752g (3.95 mol)  
16 of polyisobutene (BP Ultravis 10) and 2800g of a polyPIBSA/-  
17 polyisobutene mixture (prepared according to Example 13)  
18 which comprised about 57 weight percent polyPIBSA and about  
19 43 weight percent (1.27 mol) unreacted polyisobutene. The  
20 mixture was heated to 91°C; then 14g (0.143 mol) maleic  
21 anhydride and 2.7g (0.0185 mol) di-tert-butyl peroxide  
22 (DTBP) were added. A slight exotherm was noticed where the  
23 temperature increased to 147°C. The mixture was stirred and  
24 heated at 140°C for one hour. After standing at room tem-  
25 perature overnight, the mixture was heated to 140°C and 378g  
26 (3.86 mol) maleic anhydride and 56.7g (0.388 mol) of DTBP  
27 were added. The mixture was stirred and heated at 140°C for  
28 6.5 hours. The mixture was allowed to cool to ambient tem-  
29 perature overnight. The mixture was heated to 80°C and  
30 vacuum was applied at 28 inches Hg (vac); the temperature  
31 was increased to 200°C. The mixture was stripped at 200°C  
32 and 28 inches Hg (vac) for 2 hours to remove any unreacted  
33 maleic anhydride. Analysis of the final product by proton  
34 NMR showed that a significant amount of the polybutene

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01 methylvinylidene isomer had disappeared along with the  
02 maleic anhydride.

03

04

Example 17B

05

06 A 22-liter, 3-necked flask was charged with 8040g (8.46 mol)  
07 polyisobutene (BP Ultravis 10) and 6000g of a polyPIBSA/-  
08 polybutene mixture prepared according to Example 17A. The  
09 mixture was heated to 109°C, then 840g (8.57 mol) maleic  
10 anhydride and 126g (0.863 mol) DTBP were added. The  
11 resulting mixture was stirred and heated at 140°C for 5.25  
12 hours. The mixture was cooled to ambient temperature. The  
13 mixture was then heated to 128°C with stirring and an addi-  
14 tional 153g (1.561 mol) maleic anhydride and 23g (0.158 mol)  
15 DTBP were added. The mixture was stirred and heated at  
16 140°C for 3.5 hours and then an additional 153g (1.561 mol)  
17 maleic anhydride and 11.8g (0.0808 mol) DTBP were added.  
18 The mixture was stirred and heated at 140°C for an addi-  
19 tional 3.67 hours. The mixture was cooled to ambient  
20 temperature. The mixture was then stirred and heated at  
21 186°C for one hour while vacuum was applied to strip the  
22 unreacted maleic anhydride from the product. The product  
23 had a saponification number of 85.8 mg KOH/g. Inspection of  
24 the proton NMR spectrum of the final product indicated that  
25 the polybutene methyl vinylidene isomer was significantly  
26 depleted and that the maleic anhydride was totally consumed.

27

28

Example 18

29

30

Preparation of PolyPIBSA TETA

31

Polysuccinimide with a Low Degree of Polymerization

32

33 To a 5-liter flask equipped with a heating mantle, overhead  
34 stirrer and Dean Stark trap under nitrogen sweep, was added

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01 1000 g polyPIBSA prepared according to Example 17B  
02 (saponification number 85.8, molecular weight about 2500)  
03 and 999 g Chevron 100NR diluent oil. The mixture was heated  
04 to 60°C; then 75.78 g triethylene tetraamine (TETA) was  
05 added. The mixture was heated to 160°C and kept at tempera-  
06 ture for 4 hours. A total of 7.0 ml water was recovered  
07 from the Dean Stark trap. The reaction mixture was then  
08 maintained at 160°C under vacuum for 2 hours. The reaction  
09 mixture was allowed to cool. Obtained was 2018.2 g of  
10 product having %N=1.35.

11

12

Example 19

13

14

## Preparation of PolyPIBSA HPA

15

Polysuccinimide With a Low Degree of Polymerization

16

17 To a 5-liter flask equipped with a heating mantle, overhead  
18 stirrer and Dean Stark trap (under nitrogen sweep) was added  
19 1000 g polyPIBSA prepared according to Example 17B  
20 (saponification number 85.8 molecular weight 2500) and 932  
21 Chevron 100NR diluent oil. The mixture was heated to 60°C;  
22 to this was added 142.45 g heavy polyamine ("HPA") No. X  
23 obtained from Union Carbide Corporation. The mixture became  
24 very thick. The reaction mixture was heated to 165°C and  
25 maintained at that temperature for 4 hours; the mixture  
26 became less viscous. Then the reaction mixture was heated  
27 at 165°C under vacuum for 2 hours. The mixture was allowed  
28 to cool. Obtained was the above-identified product having  
29 %N=2.23.

30

31

Example 20 (Comparative)

32

33 An experiment was performed in a manner similar to  
34 Examples 17A and 17B, but in the absence of any added

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01 oligomeric copolymer solvent. The resulting mixture, upon  
02 heating, formed a significant amount of maleic anhydride  
03 (MA) resin, as indicated by total disappearance of the MA  
04 peak in the proton NMR, while still leaving a large amount  
05 of methyl vinylidene protons. Moreover, MA resin formation  
06 was evidenced by the product being stuck to the reactor  
07 walls and the formation of tar.

08

09

Example 21

10

Proton NMR Analysis of Reaction  
11 of Polyisobutene with MA

12

13 The reaction of PIB with MA can be monitored by proton NMR.  
14 The MA peak in deuteriochloroform is located at 7.07 ppm and  
15 the methyl vinylidene olefin hydrogens are at 4.61 and  
16 4.87 ppm. Disappearance of these peaks, especially the PIB  
17 vinylidene peaks, indicates copolymerization with the MA.  
18 IR can also be used to confirm that copolymerization is  
19 occurring. Generally, the reaction is run until the MA  
20 olefin peak disappears and the methyl vinylidene peaks have  
21 significantly decreased.

22

23

Example 22

24

Saponification Number of PIBSA and PolyPIBSA

25

26 Approximately one gram of sample is weighed and dissolved in  
27 30 ml xylene in a 250-ml Erlenmeyer flask at room tempera-  
28 ture. Unless otherwise noted, the polyPIBSA product samples  
29 were filtered at about reaction temperature to remove any MA  
30 hydrolysis product (i.e., fumaric acid) and any poly MA  
31 resin.

32

33 Twenty-five ml of KOH/methanol is added to the xylene  
34 solution. A reflux condenser is attached and the mixture is

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01 heated to reflux using a hotplate/stirrer and held at reflux  
02 for 20 minutes. A ceramic spacer is placed beneath the  
03 flask, and 30 ml of isopropyl alcohol is added through the  
04 condenser. The sample is then cooled to about room temper-  
05 ature and back titrated with 0.5 Normal HCl, using a Metrohm  
06 670 auto titrator and a Dosimat 665 pump system.

07

08 Comparisons with blanks provide the saponification number  
09 (SAP number), which is mg of KOH/gm of sample.

10

11

#### Examples 23-25

12

13 Examples 23-25 were carried out following the general  
14 procedure of Examples 16, 17A and 17B. The results are  
15 shown in Table II.

16

17 In Example 24, proton NMR showed a significant consumption  
18 of polyisobutene methyl vinylidene isomer and maleic  
19 anhydride. In Example 25, the maleic anhydride and free  
20 radical initiator were added by slugs.

21

22

#### Example 26

23

24 A reaction mixture containing 350 grams of a 45 weight  
25 percent polyPIBSA and 55 weight percent unreacted polyiso-  
26 butene mixture having a SAP Number of 34 was combined with  
27 150 grams BP ULTRAVIS 30, a high vinylidene polyisobutene  
28 having an average molecular weight of about 1300 and 176  
29 grams of a Chevron 100 neutral lubricating oil. The mixture  
30 was heated to 50°C. Twenty-two (22) grams of maleic  
31 anhydride and 5 grams of t-butylperoxy-2-ethyl hexanoate  
32 (t-butyl peroctoate) were added. The reaction temperature  
33 was raised to 90°C and held at this temperature for 4 hours.

34

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01 A product with a SAP Number of 26 was produced. Proton NMR  
02 indicated a very slow reaction rate.

03

04

Example 27

05

06 A reaction mixture containing 500 grams of a 45 weight  
07 percent polyPIBSA and 55 weight percent unreacted polyiso-  
08 butene mixture having a SAP Number of 34 was combined with  
09 214 grams BP ULTRAVIS 30, a high vinylidene polyisobutene  
10 having an average molecular weight of about 1300. The  
11 mixture was heated to 110°C and 31.4 grams of maleic  
12 anhydride was added. Every 15 minutes starting from the MA  
13 addition time, 6.53 grams of 100 neutral oil and 0.73 grams  
14 of t-butylperoxy-2-ethyl hexanoate (t-butyl peroctoate) were  
15 added. Additions were continued for the first 2 hours and  
16 30 minutes. Thereafter the reaction was held at 110°C for  
17 5.5 hours. This produced a product which had a SAP Number  
18 of 31. Proton NMR showed a slow reaction rate.

19

20

Example 28

21

22 A reaction mixture containing 464 grams of a 45 weight  
23 percent polyPIBSA and 55 weight percent unreacted polyiso-  
24 butene mixture having a SAP Number of 34 was combined with  
25 316 grams BP ULTRAVIS 30, a high vinylidene polyisobutene  
26 having an average molecular weight of about 1300. The  
27 mixture was heated to 120°C and 31.2 grams of maleic  
28 anhydride and 5.85 grams of t-butylperoxy-2-ethyl hexanoate  
29 (t-butyl peroctoate) were added. The reaction temperature  
30 was raised to and held at 120°C for 6 hours. A product with  
31 a SAP Number of 33 was produced.

32

33

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01 Example 29

02

03 A reaction mixture containing 259 grams of a 45 weight  
04 percent polyPIBSA and 55 weight percent unreacted polyiso-  
05 butene mixture having a SAP number of 34 was combined with  
06 177 grams BP ULTRAVIS 30, a high vinylidene polyisobutene  
07 having an average molecular weight of about 1300. The  
08 mixture was heated to 130°C and 12.6 grams of maleic  
09 anhydride and 3.32 grams of di-t-butylperoxide were added.  
10 The reaction temperature was held at 130°C for 5 hours.  
11 Then 5.1 grams of maleic anhydride and 0.7 grams of di-t-  
12 butylperoxide were added. The temperature was raised to  
13 140°C and then held these for 4.5 hours. The product had a  
14 SAP Number of 41. Proton NMR showed a significant reduction  
15 in polyisobutene methyl vinylidene isomer.

16

17 Example 30

18

19 A reaction mixture containing 896 grams of polyPIBSA con-  
20 taining some unreacted polybutene was combined with 1883  
21 grams BP ULTRAVIS 30. The mixture was heated to 140°C and  
22 142 grams of maleic anhydride and 21.2 grams of di-t-butyl-  
23 peroxide were added. The reaction temperature was raised  
24 and held at 140°C for 4 hours and then heated to 200°C for 2  
25 hours. The product had a SAP Number of 49.

26

27 Example 31 (Comparative)

28

29 A reactor containing 721 grams BP ULTRAVIS 30 was heated to  
30 140°C and 38.8 grams of maleic anhydride and 8.2 grams of  
31 di-t-butylperoxide were added. This reaction was done in  
32 the absence of added polyPIBSA solvent. The reaction tem-  
33 perature was held at 140°C for 7 hours. An abundance of  
34 tarry resin, believed to be derived from the maleic

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01 anhydride was evident. The mixture was filtered hot. The  
02 product had a SAP number of 17 after the resin was filtered  
03 out. The percent actives was 37%.

04

05

Example 32

06

07 This reaction shows that after the copolymer is formed,  
08 unreacted PIB can be reacted with maleic anhydride to form  
09 thermal PIBSA.

10

11 PolyPIBSA prepared in a manner similar to Example 17B having  
12 a SAP Number of 86 was charged to a reactor and heated to  
13 204°C. A molar equivalent of MA (43.3 g), relative to  
14 unreacted non-vinylidene polybutene, of MA was added and the  
15 mixture heated to 232°C and held at this temperature for  
16 4 hours. The temperature was reduced to 210°C and the  
17 pressure was reduced to 28 inches of mercury. The reduced  
18 pressure and temperature was maintained for one hour. Then  
19 the mixture was filtered. The product had a SAP Number  
20 of 88. The results of Examples 26-32 are shown in Table II.

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TABLE II

Examp	P10 MW	P10 Mole	MA Mole	Initiator Type	Init. Mole	P10 Grams	PolyP10SA Grams	Wt% P10 in Ex Mixture	Ex Temp °C	Ex Time Minutes	SAP Number	Wt% Actives
23	950	0.00	0.08	Di-t-Butyl Peroxide	0.12	0.0	100	0.0	150	300	90	71.8
24	950	3.95	4.00	Di-t-Butyl Peroxide	0.40	1752.0	2800.0	57.3	140	400	—	—
25	950	8.46	8.57	Di-t-Butyl Peroxide	0.86	8040.0	6000.0	53.5	140	620	76	77.2
26 <sup>a</sup>	1300	0.12	0.23	t-Butyl Peroctoate	0.02	150.0	350.0	22.2	90	240	26	—
27 <sup>b</sup>	1300	0.17	0.32	t-Butyl Peroctoate	0.03	214.5	500.0	27.5	110	330	31	—
28	1300	0.24	0.32	Di-t-Butyl Peroxide	0.04	315.8	463.8	40.5	120	240	33	—
29	1300	0.14	0.13	Di-t-Butyl Peroxide	0.03	176.9	259.0	40.6	130	450	41	—
30	1300	1.45	1.45	Di-t-Butyl Peroxide	0.15	1883.0	896.0	70.3	140	240	49	60.4
31	1300	0.55	0.40	Di-t-Butyl Peroxide	0.06	721.0	0.0	100.0	140	420	17	32.6
32	950	0.00	0.44	— None —	0.00	0.0	700.0	0.0	232	240	88	78.0

<sup>a</sup> The reaction mixture contained 176 grams of neutral lubrication oil (26 wt.% in reaction mixture).

<sup>b</sup> The reaction mixture contained 65.25 grams of neutral lubrication oil (8.4 wt.% in reaction mixture).

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01 WHAT IS CLAIMED IS:

02

03 1. A process for preparing an oligomeric copolymer of an  
04 unsaturated acidic reactant and a high molecular weight  
05 olefin having a sufficient number of carbon atoms such  
06 that the resulting copolymer is soluble in lubricating  
07 oil and wherein at least 20 weight percent of the total  
08 olefin comprises an alkylvinylidene isomer, which  
09 process comprises reacting the high molecular weight  
10 olefin with the unsaturated acidic reactant in the  
11 presence of a solvent which comprises the reaction  
12 product of an unsaturated acidic reactant and a high  
13 molecular weight olefin.

14

15 2. The process according to Claim 1, wherein the  
16 unsaturated acidic reactant employed to produce either  
17 the copolymer product or the solvent is of the formula:

18

19

20

21



22 wherein X and X' are each independently selected from  
23 the group consisting of -OH, -Cl, -O-lower alkyl of 1  
24 to 6 carbon atoms and when taken together, X and X'  
25 are -O-.

26

27 3. The process according to Claim 1, wherein at least 50  
28 percent of the total olefin employed to produce the  
29 copolymer product comprises an alkylvinylidene isomer.

30

31 4. The process according to Claim 1, wherein the high  
32 molecular weight olefin employed to produce either the  
33 copolymer product or the solvent has an average  
34 molecular weight of about 500 to about 5000.

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- 01 5. The process according to Claim 1, wherein the high  
02 molecular weight olefin employed to produce either the  
03 copolymer product or the solvent is polyisobutene.  
04
- 05 6. The process according to Claim 1, wherein the  
06 oligomeric copolymer produced has an average degree of  
07 polymerization of about 1.5 to about 10.  
08
- 09 7. The process according to Claim 1, wherein the acidic  
10 reactant employed to produce the copolymer product is  
11 maleic anhydride and the alkylvinylidene isomer  
12 employed to produce the copolymer product is  
13 methylvinylidene.  
14
- 15 8. The process according to Claim 1, wherein the solvent  
16 comprises the reaction product of maleic anhydride and  
17 polyisobutene.  
18
- 19 9. The process according to Claim 8, wherein the solvent  
20 comprises thermal PIBSA or chlorination process PIBSA.  
21
- 22 10. The process according to Claim 1, wherein the solvent  
23 comprises the oligomeric copolymer product of said  
24 process.  
25
- 26 11. The process according to Claim 10, wherein the solvent  
27 comprises polyPIBSA.  
28
- 29 12. The process according to Claim 1, wherein the solvent  
30 comprises either (a) an oligomeric copolymer of an  
31 unsaturated acidic reactant and a high molecular weight  
32 olefin, or (b) a monomeric adduct of an unsaturated  
33 acidic reactant and a high molecular weight olefin in  
34

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01 at least a one to one mole ratio of acidic reactant to  
02 olefin; or a mixture thereof.  
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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04282

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL <sup>4</sup> C07C 55/00, 69/34; Co7D 307/34; C10M 129/93		
U.S. CL 562/590, 596; 560/190, 204; 549/233, 252; 252/56D		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched ?		
Classification System	Classification Symbols	
U.S.	562/590, 596; 560/190, 204; 549/233, 252 252/56D	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b>		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 4,548,725 (BRIDGER) 22 October 1985	1-12
Y	See entire document	1-12
X	US, A 4,526,950 (GRAVA) 02 July 1985	1-12
Y	See entire document	1-12
X	US, A, 3,677,725 (ANDRESS, JR.) 18 July 1972	1-12
Y	See entire document	1-12
X	JP, A, 63-270671 (MITSUBISHI) 12 November 1988	1-12
Y	See entire document	1-12
A	US, A, 4,359,325 (DAWANS ET AL) 16 November 1982	1-12
	See entire document	
A	US, A, 4,055,581 (HOPKINS ET AL) 25 October 1977	1-12
	See entire document	
<p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
12 December 1989		09 FEB 1990
International Searching Authority		Signature of Authorized Officer
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